CO chemisorption at pristine, doped and defect sites on Graphene/Ni(111)

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Abstract

Due to its exceptional properties graphene (G) is considered one of the most promising materials for the future. Recently, its possible use as gas sensor has been demonstrated [1] and free standing graphene (G) has been used as a sensing element for the detection of different gases. The high sensitivity (ppm or better) is ascribed to the doping induced by adsorption and depends critically on the nature of the reactant, being lower for CO than for other poisoning species. However, the nature of the active sites is still unclear and the need for high temperature re-generation of the sensing element after adsorption suggests a chemisorption phenomenon involving either defect sites or a doping effect. This limit determines the sensitivity and the range of temperatures at which the sensor can operate.

In order to clarify these issues performed a HREELS and XPS study on the reactivity of G supported on metals towards CO adsorption. We compared the results for a strongly interaction system as G/Ni(111) and for a non-interacting system as G/Cu$_{poly}$ finding that only the former is reactive at low temperature [1,2]. Among the different configurations of G on Ni(111), we identify top-bridge graphene as the most reactive one [3].

The effect is ascribed to an intrinsic doping of the G-layer induced by the presence of the Ni substrate. This result indicates that the nature of the substrate plays an essential role in the adsorption process. In addition, since a heat of adsorption of ~0.58 eV/molecule is estimated at low coverage, we can extrapolate an equilibrium coverage of ~0.1 ML at RT under a CO partial pressure of only 10 mbar.

As a next step, we investigated the role of doping and of defects in the reactivity of the G/Ni(111) system.

In a first instance, nitrogen atoms were introduced in the G-layer by N_2^+ ion bombardment at 110 eV. n-doping allows for the formation of a second, more strongly bound moiety characterized by a CO stretch frequency of 236 meV (in addition to the vibration at 256-260 meV observed for the pristine sample) and by an initial heat of adsorption of ~0.85 eV/molecule[4]. The presence of N (in pyridinic or substitutional sites) enhances therefore significantly the chemical reactivity of G/Ni(111) towards CO by opening an additional adsorption channel.

Isolated vacancies in the pristine G/Ni(111) and G/Cupoly films were produced by low energy Ne$^+$ ions bombardment [2]. Also in this case, the latter system is totally inert, while CO adsorption at two non-equivalent sites is observed on G/Ni(111) already at 300 K. However, both the CO stretch frequencies, their intensity ratio and the observed desorption temperature around 350 K indicate that CO chemisorbs at the G/Ni(111) interface close to the vacancies rather than at the defected G layer. The red-shift of the C1s binding energy evidences that in such regions detachment of the G layer from the substrate occurs. Subsequent adsorption/desorption cycles evidence a reduction of the CO adsorption probability indicative of some healing of the defects induced by CO; therefore vacancies at G/Ni(111) are not a good candidate as active sensing site.

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